Gold Complexes with Selenium Ligands, IV[1]

Preparation, Crystal Structures and Reactions of Phosphine(selenourea)gold(I) Complexes

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(Triphenylphosphine)(selenourea)gold(I) chloride $[Ph_3PAuSeC(NH_2)_2]^+Cl^-$ (**1**) and the corresponding dppm derivative $dppm[AuSeC(NH_2)_2]_2^{2+}\ 2\,Cl^-$ (**2**) are prepared from $SeC(NH_2)_2$ and the appropriate chloro(phosphine)gold(I) complex. The reaction between **1** and aqueous Na_2CO_3 leads to the neutral complex μ-selenido{bis[(triphenylphosphine)gold(I)]} $(Ph_3PAu)_2Se$ (**3**). An analogous reaction with **2** leads to a dark red oil, which has not yet been characterized. The reaction between **3**, Ph_3PAuCl, and $AgSbF_6$ leads to the ionic complex $[(Ph_3PAu)_3Se]^+SbF_6^-$ (**4**) in good yield. X-ray structure analyses of **1**, **2**, and **3** confirm the expected linear geometry at the gold atom and reveal short intramolecular Au – Au contacts for **2** and **3**. Short nonbonding distances between the nitrogen atoms of the amino groups and the chloride ions in the crystal structures of **1** and **2** probably indicate hydrogen bonds.

In connection with our study of gold-selenium complexes[1–4], we report here the preparation of the selenourea complexes $[Ph_3PAuSeC(NH_2)_2]^+Cl^-$ (**1**), $dppm[AuSeC(NH_2)_2]_2^{2+}2Cl^-$ (**2**) (both with crystal structures) and their reactions with aqueous Na_2CO_3.

Selenourea $SeC(NH_2)_2$ has a high nucleophilicity, caused by the strong electron-donating effect of the amino groups, which is comparable with that of thiourea[5]. Many simple metal complexes of selenourea are known, but only a few crystal structures of those compounds have been published, mainly aryltellurium complexes[6,7]. In contrast to urea and thiourea, where both N and O or S bonding is possible[8], in all selenourea complexes only Se bonding was found, although most of the data were obtained from infrared spectroscopy.

The reaction of (triphenylphosphine)gold(I) chloride Ph_3PAuCl with selenourea in acetone leads directly to the precipitation of (triphenylphosphine)(selenourea)gold(I) chloride $[Ph_3PAuSeC(NH_2)_2]^+Cl^-$ (**1**) in nearly quantitative yield [eq. (1)].

$$Ph_3PAuCl + SeC(NH_2)_2 \longrightarrow \underset{\mathbf{1}}{[Ph_3PAuSeC(NH_2)_2]^+Cl^-} \qquad (1)$$

An exactly analogous reaction of $[(dppm)(AuCl)_2]$ with two equivalents of $SeC(NH_2)_2$ leads to the corresponding binuclear complex $dppm[AuSeC(NH_2)_2]_2^{2+}2Cl^-$ (**2**) [eq. (2)]. Complexes **1** and **2** are air-stable, colourless crystalline solids. They are soluble in methanol but insoluble in halogenoalkanes and acetone.

$$[(dppm)(AuCl)_2] + 2\,SeC(NH_2)_2 \rightarrow \underset{\mathbf{2}}{dppm[AuSeC(NH_2)_2]_2^{2+}2Cl^-} \qquad (2)$$

The reaction of **1** with aqueous Na_2CO_3 leads to the formation of the neutral complex μ-selenido{bis[(triphenylphosphine)gold(I)]} $(Ph_3PAu)_2Se$ (**3**) [eq. (3)].

$$1 + H_2O + Na_2CO_3 \longrightarrow \underset{\mathbf{3}}{(Ph_3PAu)_2Se} + \text{other products} \qquad (3)$$

The mechanism of this reaction is not well understood, but the precipitation of elemental selenium during the reaction probably indicates the formation of selenourea, which decomposes under these conditions. An analogous reaction of **2** with aqueous Na_2CO_3 leads to a dark red oil, which could not be crystallized. Stockel and Dumas used an inverse type of this alkaline hydrolysis for the synthesis of RSe^- complexes of gold [R = malate, tetraacetyl-β-D-glucosyl, β-D-glucosyl and (phenylcarbamoyl)methyl] from Et_3PAuCl and the corresponding isoselenuronium hydrobromides[9].

Compound **3** can be seen as a diaurated selenide with donor-ligand properties. Thus, the reaction of **3** with Ph_3PAuCl in the presence of $AgSbF_6$ leads directly to the ionic trinuclear complex $[(Ph_3PAu)_3Se]^+SbF_6^-$ (**4**) in good yield [eq. (4)].

$$3 + Ph_3PAuCl + AgSbF_6 \longrightarrow \underset{\mathbf{4}}{[(Ph_3PAu)_3Se]^+SbF_6^-} + AgCl \qquad (4)$$

This complex has been already prepared with Cl^- as counterion from Ph_3PAuCl and $Se(SiMe_3)_2$[10] and with PF_6^- as counterion from Ph_3PAuCl, $Se(SnMe_3)_2$, and $AgPF_6$[11]. The crystal structure of the PF_6^- salt is already known[11].

Compound **1** crystallizes with two independent molecules and one acetonitrile solvate in the asymmetric unit. Each molecule displays the expected linear geometry at the gold atom [176.5, 174.7(1)°] (Figure 1). The Au – Se bond lengths are 241.2(2) pm. This value lies in the middle of the published bond-length range of selenium – gold(I) complexes from 237.1(2) pm in $Ph_3PSeAuCl$[12] to 244.4 pm in the $[(Ph_3PAu)_3Se]^+$ cation (average of six bonds)[11]. The C – N bond length is 131.2(19) pm (average of four bonds) and therefore of nearly the same value as in free selenourea[13] and in the $[\{SeC(NH_2)_2\}_3]^{2+}$ ion[13]. The C – Se bond lengths are more sensitive towards complexation [191.0(16) pm in **1**; 186.7(4) pm in free selenourea[13]]. Short nonbonding N – Cl contacts (320.8 – 335.3 pm) probably indicate hydrogen bonds, but the hydrogen atoms were not refined freely.

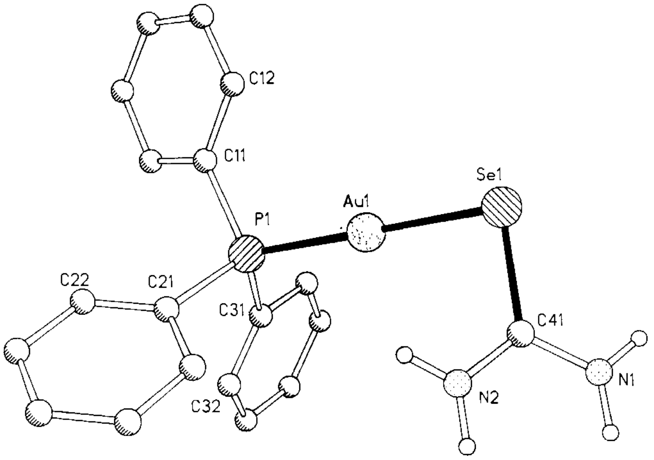

Figure 1. One of the two independent cations of compound **1**; radii are arbitrary; phenyl-H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Au – Se 241.2(2), 242.7(2), Au – P 225.9(5), 226.1(5), Se – C 190.8(16), 191.1(15), C – N 133.3(17), 130.6(21), 130.0(17), 131.0(20); Se – Au – P 176.5(1), 174.7(1), Au – – Se – C 95.0(5), 97.1(5), Se – C – N 117.9(12), 121.1(10), 118.5(12), 120.8(10), N – C – N 121.0(14), 120.6(14)

The analogous dppm derivative **2** crystallizes with one molecule and one methanol solvate in the asymmetric unit. Because of the *cis* orientation in the dication (Figure 2), the geometry at the gold atoms shows appreciable deviations from linearity [171.0, 171.8(1)°]. This *cis* orientation causes a short intramolecular gold – gold interaction of 323.6(1) pm, associated with a distorted tetrahedral geometry at the bridging carbon atom [P – C – P 115.8(5)°]. Both gold(I) – gold(I) interactions and distortions in the geometry of bridging carbon atoms in dppm complexes are well documented[14 – 17]. In the latter case, this distortion, in combination with the positive polarisation at the neighbouring phosphorus atoms, leads to an acidic character of the methylene protons[17]. The Au – Se bond lengths are 243.0(1) and 242.6(1) pm and thus only 1 pm longer than in complex **1**. The C – Se and C – N bond lengths are closely similar to those in **1**. As in the crystal structure of **1**, short N – Cl contacts (316 – 336 pm) are observed, corresponding to hydrogen bonding. Some other short nonbonding contacts [O1 – Cl2i 316.3 pm; Au1 – Cl2 336.3 pm; Au2 – Cl2 338.2 pm; i: 2 – *x*, – *y*, – *z*] in combination with the hydrogen bonds cause the arrangement of **2** in centrosymmetric pairs.

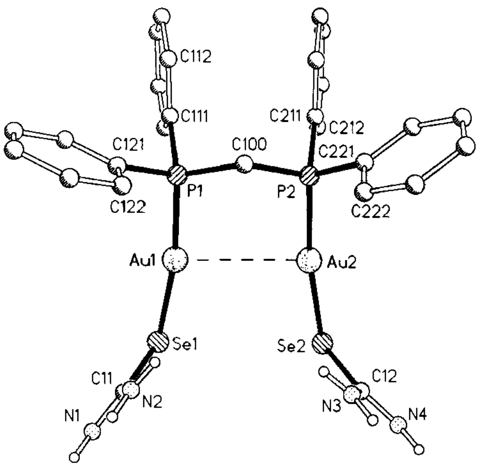

Figure 2. The dication of compound **2** (radii are arbitrary; phenyl-H atoms omitted for clarity; only one alternative position of the disordered phenyl group C221 – C226 is shown); selected bond lengths [pm] and angles [°]: Au ··· Au 323.6(1), Au – Se 243.0(1), 242.6(1), Au – P 226.5(3), 226.8(3), Se – C 190.0(10), 187.6(10), P – C(100) 182.4(11), 181.3(11), N – C 130.2(14), 131.6(14), 133.5(13), 131.7(15); Au ··· Au – Se 100.9(1), 99.5(1), Se – Au – P 171.0(1), 171.8(1), Au ··· Au – P 88.4(1), 87.7(1), Au – Se – C 101.0(3), 99.9(3), Se – C – N 117.8(7), 121.6(8), 122.5(8), 118.7(7), N – C – N 120.6(9), 118.7(9), P – C – P 115.8(5)

Compound **3** is isostructural with the analogous sulfur complex $(Ph_3PAu)_2S \cdot CH_2Cl_2$[11]. It crystallizes with one molecule and one dichloromethane solvate per asymmetric unit. Short intramolecular gold – gold contacts are observed [305.1(1) pm] (Figure 3). They give rise to an extreme distortion of ideal geometry at the selenium atom [Au – Se – Au 79.1(1)°]. The Au – Se bond lengths [239.4(1), 239.8(1) pm] are much shorter than those of the $[(Ph_3PAu)_3Se]^+$ ion (average of six bonds 244.4 pm)[11]. This is probably due to a reduced steric demand of only two triphenylphosphine groups in **3**.

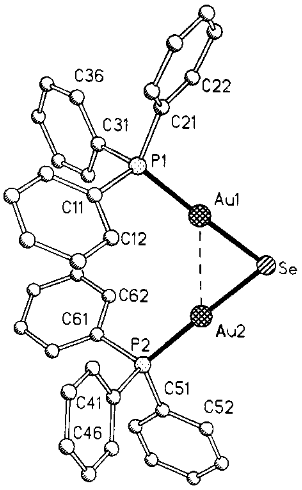

Figure 3. The molecular structure of compound **3** (radii are arbitrary; the solvent molecule and H atoms omitted for clarity); selected bond lengths [pm] and angles [°]: Au ··· Au 305.1(1), Au – Se 239.4(1), 239.8(1), Au – P 225.4(2), 225.5(2); Se – Au – P 175.0(1), 178.5(1), Au ··· Au – P 132.4(1), 131.0(1), Au – Se – Au 79.1(1)

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Experimental

All syntheses were carried out in dried solvents under nitrogen. – NMR: Bruker AC200; δ^1H relative to TMS int., δ^{31}P relative to 85% H_3PO_4 ext., δ^{77}Se relative to Me_2Se ext. – Elemental analyses: Se Fa. Beller, Göttingen, otherwise locally.

[Ph$_3$PAuSeC(NH)$_2$)$_2$]$^+$Cl$^-$ (**1**): Ph_3PAuCl (996 mg, 2 mmol) is dissolved in 100 ml of acetone and added with stirring to a solution of $SeC(NH_2)_2$ (246 mg, 2 mmol) in 50 ml of acetone. After 10 min, a white precipitate is formed; the resulting suspension is stirred for 1 h. After evaporation to dryness, the amorphous product can be recrystallized from 100 ml CH_3CN/5 ml CH_3OH at 70°C. The yield is 1.2 g (97%) of the colourless product **1**; m.p. 181 °C (dec.) – ^{1}H NMR [$CD_3OD/CDCl_3$ (10:1)]: δ = 4.4 (s, 4H, NH), 7.15 (m, 6H, *o*-H), 7.3 (m, 9H, *m*- and *p*-H). – ^{31}P NMR [$CD_3OD/CDCl_3$ (10:1)]: δ = 40 (s). – ^{77}Se NMR [$CDCl_3/CD_3OD$ (10:1)]: δ = 217 (d, $^2J_{Se,P}$ = −13 Hz).

$C_{19}H_{19}AuClN_2PSe$ (617) Calcd. C 36.96 H 3.10 N 4.54 Se 12.74
Found C 36.97 H 3.19 N 5.14 Se 13.08

dppm[AuSeC(NH$_2$)$_2$]$_2^{2+}$2Cl$^-$ (**2**): In an exactly analogous reaction, a suspension of dppm$(AuCl)_2$ (848 mg, 1 mmol) in 50 ml of acetone is added with stirring to a solution of $SeC(NH_2)_2$ (246 mg, 2 mmol) in 100 ml of acetone. After recrystallization from CH_3CN/CH_3OH at 70°C, the yield of colourless crystals of **2** is 600 mg (53%); m.p. 177°C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 4.74 (t, $^2J_{H,P}$ = 13 Hz, 2H, CH_2), 7.41 (m, 12H, *m*- and *p*-H), 7.76 (m, 8H, *o*-H), 8.62 (s, 4H, NH), 8.86 (s, 4H, NH). – ^{31}P NMR ([D$_6$]DMSO): δ = 33.7 (s). – ^{77}Se NMR ([D$_6$]DMSO): δ = 214 (d, $^2J_{Se,P}$ = −13 Hz).

$C_{27}H_{30}Au_2Cl_2N_4P_2Se_2$ (1095): Calcd. C 29.62 H 2.76 N 5.12
Found C 29.75 H 2.97 N 4.82

(Ph$_3$PAu)$_2$Se · CH$_2$Cl$_2$ (**3**): A solution of Na_2CO_3 (508 mg, 4.8 mmol) in 20 ml of H_2O is added with stirring to a solution of **1**

Table 1. Crystal data for **1**, **2**, and **3**

	1	**2**	**3**
Formula*	$C_{19}H_{19}AuClN_2PSe$	$C_{27}H_{30}Au_2Cl_2N_4P_2Se_2$	$C_{36}H_{30}Au_2P_2Se$
M_r*	617.5	1094.8	997.2
Crystal habit	Colourless plate	Colourless prism	Colourless prism
Crystal size (mm)	0.38 x 0.2 x 0.05	0.2 x 0.12 x 0.16	0.16 x 0.2 x 0.56
Space group	Pbca	$P\bar{1}$	$P2_1/c$
Temperature (°C)	-95	-95	-95
Cell constants:			
a (pm)	1181.9(2)	1099.8(2)	879.2(2)
b (pm)	2423.9(3)	1196.5(2)	2205.3(6)
c (pm)	3066.6(5)	1319.5(2)	1857.6(5)
α (°)		77.15(1)	
β (°)		89.58(1)	97.08(2)
γ (°)		83.94(1)	
V (nm^3)	8.785	1.683	3.574
Z	16	2	4
D_x (Mg m^{-3})	1.93	2.16	2.00
F (000)	4848	1056	2040
μ (mm^{-1})	8.4	10.9	9.4
2Θ max (°)	45	50	50
No. of reflections:			
measured	10990	9109	16853
independent	5724	5917	6293
R_{int}	0.088	0.022	0.027
observed [$>4\sigma(F)$]	3169	4064	4120
Absorption correction	DIFABS	DIFABS	ψ-Scans
Transmissions	0.82-1.31	0.88-1.19	0.52-0.84
R	0.046	0.040	0.032
wR	0.043	0.043	0.035
g	0.0002	0.00035	0.00025
No. of parameters	273	190	140
S	1.0	1.2	1.2
Max. Δ/σ	0.496	0.002	0.001
Max. $\Delta\rho$ (10^{-6} e pm^{-3})	1.6	1.9	1.1

* Without solvent molecule.

Table 2. Atom coordinates (× 10^4) and equivalent isotropic temperature factors (× 10^{-1}) [pm^2] for compound **1**

	x	y	z	U(eq)
Au(1)	6887.1(6)	5120.9(2)	6728.7(3)	30(1)
Se(1)	6397(1)	5574.4(4)	7402.7(6)	27(1)
P(1)	7424(4)	4665(2)	6120(2)	34(2)
Cl(1)	4370(3)	4575(2)	7366(2)	34(2)
C(11)	6491(14)	4096(6)	5994(6)	30(4)
C(12)	5727(17)	3919(7)	6317(7)	47(5)
C(13)	5019(17)	3480(7)	6233(7)	50(5)
C(14)	5053(17)	3233(7)	5824(7)	46(5)
C(15)	5794(17)	3377(7)	5515(7)	53(6)
C(16)	6511(15)	3831(6)	5595(6)	35(4)
C(21)	8848(14)	4415(6)	6173(5)	28(4)
C(22)	9275(17)	3955(7)	5967(6)	49(5)
C(23)	10402(17)	3786(8)	6025(7)	54(6)
C(24)	11116(17)	4093(7)	6282(6)	44(5)
C(25)	10707(18)	4552(7)	6485(7)	55(6)
C(26)	9577(16)	4707(7)	6452(7)	51(6)
C(31)	7445(14)	5088(6)	5630(5)	26(4)
C(32)	8398(18)	5211(8)	5411(7)	61(6)
C(33)	8307(20)	5547(8)	5030(7)	70(6)
C(34)	7308(16)	5740(7)	4897(6)	46(5)
C(35)	6315(18)	5621(7)	5097(6)	52(5)
C(36)	6391(17)	5281(7)	5487(6)	49(5)
C(41)	7657(14)	6066(6)	7396(6)	26(4)
N(1)	7449(12)	6606(4)	7418(4)	32(5)
N(2)	8692(11)	5879(5)	7379(5)	38(5)
Au(2)	3369.9(5)	7480.5(2)	6712.0(2)	29(1)
Se(2)	2255(1)	8031.9(2)	7213.5(6)	29(1)
P(2)	4407(4)	7034(2)	6203(2)	31(2)
Cl(2)	4984(4)	7077(2)	7575(2)	41(2)
C(51)	4031(15)	6317(6)	6115(6)	34(5)
C(52)	3617(15)	6124(7)	5724(6)	40(5)
C(53)	3284(16)	5578(7)	5671(7)	52(5)
C(54)	3429(15)	5209(7)	6023(6)	42(5)
C(55)	3860(16)	5396(7)	6389(7)	54(6)
C(56)	4175(16)	5951(7)	6460(7)	44(5)
C(61)	5911(13)	7033(6)	6314(5)	24(4)
C(62)	6610(16)	6602(7)	6170(6)	44(5)
C(63)	7792(17)	6666(7)	6225(6)	48(5)
C(64)	8203(18)	7121(7)	6413(6)	54(5)
C(65)	7558(16)	7548(7)	6572(6)	49(5)
C(66)	6405(15)	7495(7)	6514(6)	40(4)
C(71)	4267(15)	7381(6)	5676(6)	35(5)
C(72)	5219(14)	7525(6)	5437(6)	34(4)
C(73)	5099(17)	7841(7)	5058(6)	46(5)
C(74)	3990(16)	7977(7)	4916(6)	44(5)
C(75)	3076(17)	7822(7)	5146(6)	45(5)
C(76)	3187(15)	7530(6)	5543(6)	41(5)
C(81)	3417(13)	8545(5)	7365(5)	21(4)
N(3)	3134(11)	9056(5)	7438(5)	35(5)
N(4)	4469(11)	8384(5)	7409(5)	37(6)
N(11)	1076(18)	6206(8)	6532(7)	96(7)
C(111)	790(39)	6267(17)	6006(15)	186(18)
C(112)	958(35)	6722(17)	5976(13)	169(16)

(2.48 g, 4 mmol) in 30 ml of CH_3OH at −10°C. The colour changes immediately to yellow. After stirring for 1 h at −10°C, a yellow solid precipitates. After warming up to room temperature in 3 h and stirring at 40°C for 1 h, 50 ml of CH_2Cl_2 is added. The organic layer is separated, and the aqueous layer is extracted twice with 50 ml of CH_2Cl_2. The organic layers are combined, dried with anhydrous $MgSO_4$, and evaporated to dryness. The yellow residue is recrystallized from CH_2Cl_2/CH_3OH, leaving 1.87 g (86%) of pale yellow crystals; m.p. 152°C (dec.). — ^1H NMR ($CDCl_3$): δ = 5.3 (s, 2H, CH_2Cl_2), 7.37 (m, 30H, *o*-, *m*, and *p*-H). — ^{31}P NMR ($CDCl_3$): δ = 37.3 (s).

$C_{37}H_{32}Au_2Cl_2P_2Se$ (1082): Calcd. C 41.07 H 2.98 P 5.72
Found C 41.09 H 2.93 P 5.73

[(Ph₃PAu)₃Se]⁺SbF₆⁻ (4): Solid $AgSbF_6$ (172 mg, 0.5 mmol) is added with stirring to a solution of Ph_3PAuCl (248 mg, 0.5 mmol) and **3** (541 mg, 0.5 mmol) in 100 ml of CH_2Cl_2/diethyl ether (3:2). After 1 h stirring in the dark, the precipitated AgCl is removed by filtering through $SiO_2/MgSO_4$. The remaining solution is concentrated to 30 ml in a rotary evaporator, whereupon addition of petroleum ether causes crystallization. After recrystallization from CH_2Cl_2/petroleum ether, the yield of brown crystals is 600 mg (71%); m.p. 193°C (dec.). — ^{31}P NMR ($CDCl_3$): δ = 34.7 (s). — ^{77}Se NMR ($CDCl_3$): δ = −227 (s).

$C_{54}H_{45}Au_3F_6P_3SbSe$ (1692) Calcd. C 38.33 H 2.68 P 5.49 Se 4.65
Found C 39.03 H 3.01 P 5.44 Se 4.49

Table 3. Atom coordinates (× 10^4) and equivalent isotropic temperature factors [pm^2] for compound **2**

	x	y	z	U(eq)
Au(1)	6472.5(4)	1155.6(4)	1509.5(3)	257(2)
Au(2)	6413.8(4)	3306.7(4)	2629.7(3)	298(2)
Se(1)	8601(1)	972(1)	1005(1)	357(4)
Se(2)	8536(1)	3689(1)	2431(1)	362(4)
P(1)	4441(3)	1153(2)	1801(2)	233(9)
P(2)	4381(3)	3201(3)	2867(2)	267(10)
Cl(1)	10298(3)	6683(2)	3383(2)	348(10)
Cl(2)	6857(3)	594(2)	4106(2)	366(10)
N(1)	10157(9)	-1032(8)	1608(7)	401(36)
N(2)	8641(9)	-871(8)	2765(7)	407(37)
N(3)	8619(8)	2511(7)	4543(6)	321(33)
N(4)	9852(8)	3959(8)	4119(7)	377(37)
C(11)	9186(10)	-463(9)	1890(8)	289(25)
C(12)	9033(10)	3358(9)	3833(8)	272(25)
C(100)	3947(10)	1774(9)	2899(8)	281(25)
C(112)	2208(7)	1921(7)	737(5)	497(34)
C(113)	1500	2474	-140	509(35)
C(114)	2064	2982	-1052	557(37)
C(115)	3336	2937	-1087	1218(75)
C(116)	4044	2385	-210	771(48)
C(111)	3480	1877	702	227(23)
C(122)	4004(9)	-912(8)	3177(6)	719(45)
C(123)	3644	-2023	3413	789(49)
C(124)	3247	-2507	2621	732(46)
C(125)	3211	-1880	1593	751(47)
C(126)	3571	-769	1357	605(40)
C(121)	3967	-285	2149	335(27)
C(212)	3944(5)	4942(7)	1080(6)	494(34)
C(213)	3201	5709	327	685(44)
C(214)	1931	5738	388	321(27)
C(215)	1405	4999	1202	512(35)
C(216)	2149	4232	1955	577(38)
C(211)	3418	4203	1894	240(24)
C(221)	3733(14)	3347(12)	4125(8)	277(64)
C(222)	3985	2509	5040	267(52)
C(223)	3569	2720	5988	276(52)
C(224)	2902	3769	6022	347(58)
C(225)	2650	4607	5107	447(67)
C(226)	3066	4396	4159	326(59)
C(22A)	3978(14)	3591(12)	4089(9)	146(54)
C(22B)	4260	4644	4261	334(60)
C(22C)	3892	4979	5173	327(59)
C(22D)	3243	4262	5913	460(72)
C(22E)	2961	3209	5740	643(89)
C(22F)	3329	2873	4828	368(62)
O(1)	11442(8)	1159(8)	4207(7)	572(25)
C(1)	10763(13)	521(12)	3667(10)	570(38)

Table 4. Atom coordinates (× 10^4) and equivalent isotropic temperature factors [pm^2] for compound **3**

	x	y	z	U(eq)
Au(1)	2058.2(3)	1821.5(1)	3130.4(2)	223(1)
Au(2)	1897.7(3)	3203.3(1)	3154.7(2)	219(1)
Se	427.1(8)	2494.6(4)	2375.0(4)	250(2)
P(1)	3407(2)	1144(1)	3861(1)	228(7)
P(2)	3257(2)	3889(1)	3869(1)	244(7)
C(12)	1989(5)	1602(2)	5005(2)	330(20)
C(13)	1769	1666	5732	355(21)
C(14)	2772	1386	6272	464(24)
C(15)	3995	1041	6084	407(22)
C(16)	4215	977	5357	333(19)
C(11)	3212	1257	4818	244(17)
C(22)	2857(6)	167(2)	2941(2)	367(20)
C(23)	2297	-406	2730	432(22)
C(24)	1628	-769	3220	516(25)
C(25)	1520	-559	3920	425(22)
C(26)	2080	14	4131	334(20)
C(21)	2749	377	3641	235(17)
C(32)	6269(5)	1641(2)	3736(3)	313(19)
C(33)	7859	1628	3751	374(21)
C(34)	8648	1080	3854	412(22)
C(35)	7846	545	3943	342(20)
C(36)	6256	557	3927	305(19)
C(31)	5467	1105	3824	226(17)
C(42)	2663(6)	3396(2)	5167(3)	354(20)
C(43)	2146	3394	5847	416(22)
C(44)	1607	3928	6128	394(21)
C(45)	1585	4464	5729	371(21)
C(46)	2102	4466	5049	300(19)
C(41)	2641	3932	4768	273(18)
C(52)	1685(5)	4822(2)	3128(3)	356(21)
C(53)	1461	5412	2863	382(21)
C(54)	2643	5836	2979	409(22)
C(55)	4050	5670	3360	406(22)
C(56)	4274	5081	3625	322(19)
C(51)	3092	4657	3509	226(16)
C(62)	5943(5)	3427(2)	3479(2)	327(19)
C(63)	7514	3307	3560	360(20)
C(64)	8436	3494	4186	464(24)
C(65)	7788	3801	4730	473(24)
C(66)	6218	3920	4649	380(21)
C(61)	5296	3733	4023	251(17)
Cl(1)	5483(5)	2401(1)	1796(2)	1001(17)
Cl(2)	6771(7)	2736(2)	459(3)	1541(27)
C(1)	6863(19)	2291(7)	1075(9)	1244(59)

X-ray Structure Determinations[18]: See Table 1 for detailed crystal data. Intensity data were registered with a Siemens four-circle diffractometer using monochromated Mo-K_α radiation (ω scans). Cell constants were refined from setting angles of 50 reflexions in the range 2θ = 20−25°. Structures were solved by the heavy-atom method and subjected to full-matrix least-squares refinement [for **1**, Au, Se, P, Cl, N anisotropic and solvent isotropic without H atoms; for **2**, Au, Se, P, Cl, N anisotropic, phenyl groups idealized and solvent isotropic without H atoms, one phenyl group statically disordered (alternative positions C221−226 and C22A−22F); for **3**, Au, Se, P anisotropic, idealized phenyl groups and solvent anisotropic without H atoms]; H atoms included by using a riding model. Weighting schemes were of the form $w^{-1} = \sigma^2(F) + gF^2$. Final atomic coordinates are given in Tables 2−4.

CAS Registry Numbers

1 · ½ MeCN: 137039-52-2 / **2** · MeOH: 137039-54-4 / **3**: 137039-56-6 / **4**: 137039-57-7 / Ph_3PAuCl: 14243-64-2

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[18] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the depository number CSD-55723, the names of the authors, and the journal citation.

[326/91]